

AD-A113 899

CORNELL UNIV ITHACA NY
CLUSTER-TYPE SUPERCONDUCTING TERNARIES.(U)
JAN 82 M J SIENKO

F/6 20/3

AFOSR-80-0009

UNCLASSIFIED

AFOSR-TR-82-0313

NL

1 OF 1
AD-A
13409



END
DATE
FILMED
105-82
DTIC

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(4)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 82-0818	2. GOVT ACCESSION NO. A113899	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CLUSTER-TYPE SUPERCONDUCTING TERNARIES		5. TYPE OF REPORT & PERIOD COVERED Interim Report 1/1/81 - 12/31/81
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M.J. Sienko		8. CONTRACT OR GRANT NUMBER(s) AFOSR 80-0009
9. PERFORMING ORGANIZATION NAME AND ADDRESS Cornell University Ithaca, New York 14853		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F Project 2306/C1
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NE Bolling AFB, Building 410 Washington, D.C. 20332		12. REPORT DATE 7 January 1982
		13. NUMBER OF PAGES 8 pp.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <div style="display: flex; justify-content: space-between;"> <div> superconductivity magnetic order Chevrel phases </div> <div> borides sulfides selenides </div> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new series of rare earth osmium-iridium tetraborides has been synthesized, characterized by X-ray diffraction, and studied for magnetic susceptibility over the range 1.8 to 1100K. Several mixed Chevrel phase systems have been studied for superconductivity and crystallography as a function of replacement and nonstoichiometry.		

DTIC
ELECTE
S **APR 27 1982** **D**
E

AD A113899

DTIC FILE COPY

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

82 04 26 143

AFOSR-TR- 82-0313

CLUSTER-TYPE SUPERCONDUCTING TERNARIES

by

M.J. Sienko, Cornell University

7 January 1982



Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

INTERIM REPORT (January 1, 1981 - December 31, 1981)

Grant No. AFOSR 80-0009

Project 2306/C1

Research sponsored by the Air Force Office of Scientific Research,

Air Force Systems Command, United States Air Force.

This document has been approved for public release;
its distribution is unlimited.

Approved for public release;
distribution unlimited.

SUMMARY

The objective of this research is to make new superconducting ternary compounds and determine how the superconducting properties are affected by changes in stoichiometry and microstructure. The approach is to synthesize from ultrapure starting materials ternary borides, sulfides, and selenides of the 2nd and 3rd row transition elements, characterize the new compounds for structure, electric and magnetic behavior, and then compare with perturbed materials. A special aim is to uncover the influence of magnetic substitution and deviation from stoichiometry and how these may be controlled to enhance high critical fields and high critical temperatures.

The most important accomplishments during the report period were:

(1) synthesis and characterization of a new series of rare earth osmium-iridium borides, (2) magnetic and superconducting study over the whole pseudobinary system YbMo_6S_8 - YbMo_6Se_8 , where we showed that the literature is wrong in reporting superconductivity for the selenide and member of the series, (3) mapping out the superconductivity behavior in the pseudoternary system $(\text{Y}, \text{Lu}, \text{Th})\text{Rh}_4\text{B}_4$, (4) working out the crystal chemistry and its effect on superconductivity in lithium-intercalated niobium disulfide, (5) major reconstruction and computerizing of our low-temperature Faraday apparatus, (6) construction and successful use of a high-pressure cell for our Meissner apparatus, (7) T_c studies as a function of composition on seven Chevrel phase systems involving lanthanum, ytterbium, europium, and samarium. The details of these findings are as follows:

- (1) (Kurt Hiebl and Peter Rogl) The crystal structure of NdOs_4B_4 was refined as the NdCo_4B_4 -type structure. Complete solid solution was found for mixed crystals LaOs_4B_4 - LaIr_4B_4 . Magnetic susceptibility studies over the range 1.8-1100 K showed that $[\text{Pr}, \text{Nd}][\text{Os}, \text{Ir}]_4\text{B}_4$ compounds are characterized by Van Vleck paramagnetism of closely spaced multiplets. For the $\text{La}[\text{Os}, \text{Ir}]_4\text{B}_4$ series, a small (constant) paramagnetic moment of $0.1\mu_B$ was derived, possibly attributable to the lanthanum. In the case of PrIr_4B_4 ferromagnetic ordering was observed at very low temperature. No superconductivity was found down to 1.5 K. The new

ternary metal borides, EuOs_4B_4 and EuIr_4B_4 , were synthesized, found to have the NdCo_4B_4 -type structure, and magnetism corresponding to free Eu^{2+} ions. Complete solid solution was found in the series CeOs_4B_4 - CeIr_4B_4 with magnetic behavior changing from that of a pure Ce^{4+} state for the osmium compound to Ce^{3+} for the iridium.

- (2) (David Johnson and Jean-Marie Tarascon) The pseudobinary systems YbMo_6S_8 - YbMo_6Se_8 were investigated for magnetic and superconducting behavior to find out why, of the rare earth molybdenum chalcogenides, ytterbium is anomalously high in the sulfide series and anomalously low in the selenide series. The superconducting critical temperatures showed a monotonic decrease from 8.65 K for the fully sulfided member to <1.6 K for all selenium, but Faraday susceptibility studies showed more magnetic ion (3.3% Yb^{3+}) in the sulfide than in the selenide (1.3% Yb^{3+}). Superconductivity of the selenide as erroneously reported in the literature over the range 4.7-5.8 K could be reproduced with nonstoichiometric material $\text{Yb}_{1+x}\text{Mo}_6\text{Se}_8$ ($T_c = 5.6 - 5.8$ K) but X-ray studies showed presence of a second phase corresponding to Mo_6Se_8 , which normally has $T_c = 6$ K.
- (3) (Kurt Hiebl and Peter Rogl) Superconductivity was studied in the pseudoternary system YRh_4B_4 - LuRh_4B_4 - ThRh_4B_4 as nonmagnetic analogs of RERh_4B_4 . Isocritical temperatures as well as isochores were established. A minimum critical temperature was found in the pseudobinary system $\text{Y}_x\text{Lu}_{1-x}\text{Rh}_4\text{B}_4$ at 10.1 K and $x = 0.5$. The pair-breaking influence of magnetic RE ions was worked out in good agreement with the Abrikosov-Gorkov theory for isotropic elastic exchange scattering of conduction electrons by randomly distributed and noninteracting localized magnetic moments.

- (4) (Craig McEwen) Ultra-pure samples of Li_xNbS_2 in the range $0 < x < 0.67$ were synthesized by high temperature reaction of Li_2S , Nb, and S. Lattice parameters were characterized from Debye-Scherrer and single-crystal rotation photographs. Superconducting critical temperatures, measured by a.c. mutual inductance, showed a totally unexpected triple alternation of decreasing and increasing critical temperatures with successive maxima at $x = 0$, 0.10, and 0.33. The predominant polytype changed from 2H to 3R back to 2H again as x was increased. Results have been interpreted in terms of the effect of intercalation on the charge-density-wave transition.
- (5) (Dave Johnson and Dell St. Julien) A Janis "Super Varitemp" Cryostat equipped with integrally mounted liquid helium level sensing probe and GaAs temperature sensor was installed as the replacement for the leaking Dewar in the Faraday Magnetic Susceptibility Assembly. The manual electronic controls for temperature and field changes have been replaced by a microprocessor for automatic data acquisition. Programs have been developed for free-running, single-cycle, and complete micro control. Most important, as calibrated by runs on known materials, the new system works!
- (6) (Dave Johnson) The Meissner coils have been rewound and a new stainless steel pressure cell of the torque type capable of generating 10 Kbar has been constructed. Preliminary calibrations on known superconducting materials indicate that we can reach 7 Kbar.
- (7) (Dave Johnson and Jean-Marie Tarascon) Structure and superconductivity studies on the pseudobinary system $\text{LaMo}_6(1-x)\text{Se}_x$ show that the c/a ratio has a minimum at $x = 0.75$ but T_c has its minimum (1.6 K) at $x = 0.3$. Apparently the selenium atoms preferentially occupy the general position sites on the $\bar{3}$ axis. For the pseudobinary system $\text{La}_{1-x}\text{Yb}_x\text{Mo}_6\text{Se}_8$ the T_c remains relatively high (10-11 K) for

$x < 0.5$ but then drops off rapidly to less than 1.5 K for $x = 0.1$. For the $\text{La}_{1-x}\text{Yb}_x\text{Mo}_6\text{S}_8$ system, the T_c remains roughly constant at 6.5 K for $0 < x < 0.8$ and then rises rapidly to 8.65 K for YbMo_6S_8 . The results can be explained by changes in the density of states at the Fermi level due to variation in the extent of band filling (going from divalent to trivalent metal) and narrowing of the band width (going from sulfide to selenide). For the six systems studied $\text{MMo}_6\text{S}_{8-x}\text{Se}_x$ ($M = \text{Yb}, \text{Eu}, \text{Sm}, \text{Pb}, \text{La}, \text{Ag}$) the c/a ratio is found to have its minimum at around the midpoint ($x = 4$) except for lanthanum ($x = 6$). It is believed that ordering of the chalcogen occupancy by M^{3+} is greater than that by M^{2+} or M^+ . Delocalization of the M^{n+} away from the $\bar{3}$ axis apparently decreases the ordering since it tends to increase the bonding in the a direction.

PERSONNEL

In addition to the principal investigator, Professor M.J. Slenko, the following people were associated with this project during various parts of the report period:

(a) Postdoctoral Research Associates

Dr. Jean-Marie Tarascon (January - December)
Dr. Kurt Hiebl (March)
Dr. Peter Rogl (July - August)

(b) Research Assistants

Dave Johnson (January - December)
Craig McEwen (January - June)
Eric Bell (January - June)
Dell St. Julien (July - August)

One Ph.D. degree was completed during this period, that of Angelica Stacy on "The Metal-Insulator Transition in Lithium Metal Solutions". (Primary sponsor NSF).

PUBLICATIONS

The following papers containing AFOSR acknowledgment were published or accepted for publication during the report period:

"Hf(Se_{1-x}Te_x)₂: Deviations from Vegard's Law in Mixed Systems." D.T. Hodul and M.J. Slenko. Inorg. Chem. 20 3655-3659 (1981).

"Magnetic Behavior and Structural Chemistry of RE(Os,Ir)₄B₄-Borides." K. Hiebl, P. Rogl, and M.J. Slenko. J. Less-Common Metals 82 21-28 (1981).

"Phase Separation in Metal Solutions and Expanded Fluid Metals." P.P. Edwards and M.J. Slenko, J. Am. Chem. Soc. 103 2967-2971 (1981).

"Temperature-Dependent Electron Spin Interactions in Lithium [2.1.1] Cryptate Electride Powders and Films." J.S. Landers, J.L. Dye, A. Stacy, and M.J. Slenko, J. Phys. Chem. 85 1096-1099 (1981).

"Superconductivity in the Pseudoternary System YRh₄B₄-LuRh₄B₄-ThRh₄B₄." K. Hiebl, P. Rogl, and M.J. Slenko. J. Less-Common Metals accepted for Vol. 82.

"Ambivalent Behavior of Ytterbium in the Pseudobinary System YbMo₆S₈-YbMo₆Se₈." J.-M. Tarascon, D.C. Johnson, and M.J. Slenko. Inorg. Chem. accepted for March 1982.

"Structural Chemistry and Magnetic Properties of the Compounds EuOs₄B₄ and EuIr₄B₄ and of the Solid Solutions REOs₄B₄-REIr₄B₄ (RE = Ce, Pr, Sm)." K. Hiebl, P. Rogl, and M.J. Slenko. Inorg. Chem. accepted for March 1982.

"The Transition to the Metallic State." P.P. Edwards and M.J. Slenko. Accounts of Chem. Research accepted for March 1982.

"Conductivity Studies in Search of Liquid-Liquid Phase Separation by Solutions of Lithium in Methylamine." R. Hagedorn and M.J. Slenko. J. Phys. Chem. accepted for April 1982.

"Re-evaluation of the Crystal Structure Data on the Expanded-Metal Compounds $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{ND}_3)_4$." A.M. Stacy and M.J. Sienko. Inorg. Chem. accepted for April 1982.

"Low-Temperature Magnetic Susceptibility of the Expanded-Metal Compounds $\text{Li}(\text{NH}_3)_4$, $\text{Li}(\text{ND}_3)_4$, and $\text{Li}(\text{CH}_3\text{NH}_2)_4$." A.M. Stacy and M.J. Sienko. J. Chem. Phys. accepted for April 1982.

INTERACTIONS

- Lecture at ACA Symposium, American Crystallographic Association, College Station, Texas, on "Bizarre Structural Correlations of Superconductivity and Magnetism in Metal Cluster Compounds" (3/26/81).
- Visit to Bell Labs and give seminar on "Chevrel Phases" (5/21/81).
- Seminar at University of Linz on "Rare Earth Borides" (6/1/81).
- Seminar at University of Vienna on "Superconductivity and Magnetism of Complex Borides" (6/4/81).
- Lecture at University of Uppsala, Seventh International Symposium on Boron, Borides, and Related Compounds, on "Magnetic Behavior and Structural Chemistry of $\text{RE}(\text{Os, Ir})_4\text{B}_4$ -Borides" (6/9/81).
- Lecture at University of Uppsala, Symposium on Boron, on "Magnetism and Superconductivity in the Ternary System Metal-Rhodium-Boron" (6/12/81).
- Seminar at Cambridge University on "Superconducting Clusters" (6/15/81).
- Paper at CNRS Colloquium on Chemistry and Physics of Sulfides at University of Paris on "Quirks in the Superconducting Behavior of Lithium-Intercalated Niobium Disulfide" (9/15/81).
- Paper at CNRS Colloquium on Sulfides at University of Paris on "Structural, Magnetic, and Superconducting Properties of the Pseudobinary System YbMo_6S_8 - YbMo_6Se_8 " (9/16/81).
- Lecture at Cornell on "Chemical Control of Superconductivity" (10/7/81).

In addition we have had visits to discuss research with my research group at Cornell during the year as follows: Kurt Hiebl (Univ. of Vienna), Peter Edwards (Cambridge Univ.), Peter Rogl (Univ. of Vienna), Gilles LeFlem (Univ. of Bordeaux), Ulrich Schindewolf (Univ. of Karlsruhe), A. Voronel (Tel Aviv Univ.), Art Thompson (Exxon), Pierre Courtine (Univ. of Compiègne), Joshua Jortner (Tel Aviv Univ.), Frank Delk (Monsanto), Yves Chabre (Grenoble), John Steeds (Univ. of Bristol), David Baird (Ford Motor Co.), Dean Douglass (Bell Labs).

DATE
FILMED
-8